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SYNTHETIC ORGANIC CHEMICALS

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Cellulose Mixed Esters

THE physical and chemical properties of cellulose mixed esters, a number of which are now available in commercial or semicommercial quantities, are of considerable interest to those who have possible industrial uses for such materials. These compounds comprise the class of cellulose derivatives in which some of the hydroxyl groups of the cellulose have been esterified with acetic acid and some with a higher acid. These esters are uniform in composition and are not equivalent to mechanical mixtures of the cellulose esters of the individual acids.

It should be stressed that wide variations in chemical composition and in physical properties are possible within each type of cellulose mixed ester. Differences in chemical composition are due to changes in the ratio of combined acyl groups and in the degree of esterification of the cellulose. For example, cellulose acetate butyrates are those mixed esters in which the cellulose has been esterified with acetic acid (acetyl) and butyric acid (butyryl). The proportion of acetyl to butyryl may be varied from a very large quantity of acetyl with a small amount of butyryl, to a very high content of butyryl with a minor quantity of acetyl in the mixed ester.

Moreover, a cellulose acetate butyrate having any ratio of acetyl and butyryl groups may be fully esterified, i.e., a cellulose triester, or it may be partially hydrolyzed. These changes in chemical

composition result in corresponding variations in physical properties.

The principal change of a physical nature is represented by viscosity. In each of the compositions that are possible the viscosity may be varied over a fairly wide range. The choice of the particular viscosity will depend on the application for which the product is intended and the method of use.

Choice of Mixed Ester

The cellulose acetate propionates and cellulose acetate butyrates are the most practical types for purposes where mixed esters of fatty acids of comparatively low molecular weight are desired. These esters are satisfactory for most requirements of increased moisture resistance and wider solubilities.

In extreme cases, it may be necessary to employ a mixed ester containing a large quantity of an acid of very high molecular weight. For these purposes cellulose acetate palmitates or acetate stearates are the most suitable. Commercial stearic acid, which is a mixture of palmitic and stearic acids, is the most satisfactory source of the higher acid in this case. The higher acyl radical in these esters may be introduced in quantities as great as 40-45% of the total composition, the acetyl content becoming correspondingly less as the amount of the higher acyl increases.

Accurate determination of the value of cellulose mixed esters for a specific

purpose is usually most conveniently accomplished by means of testing representative samples having moderate amounts of higher acyl. Cellulose acetate propionates and cellulose acetate butyrates having 15-20% propionyl or butyryl, respectively, are very often satisfactory. In conducting any tests, however, it should be borne in mind that the samples represent only one composition out of a wide variety of possibilities, and that variations in certain characteristics may be obtained by changing the amount of higher acyl, by effecting partial hydrolysis, or by modifying the viscosity. Such treatments produce marked changes in the properties of the ester.

The introduction of greater quantities of the higher acyl results in increased moisture resistance, wider latitude of solubility, improved compatibility with resins, gums, and plasticizers, and increased electrical resistance. Simultaneously, however, there is some loss in tensile strength and in surface hardness; and films coated from such materials are somewhat less rigid.

Fully esterified esters tend to be more soluble in hydrocarbon and halo-

cizers, to flow under heat and pressure and give satisfactory molding behavior.

Cellulose acetate stearate is particularly recommended for purposes in which other cellulose esters have been found to

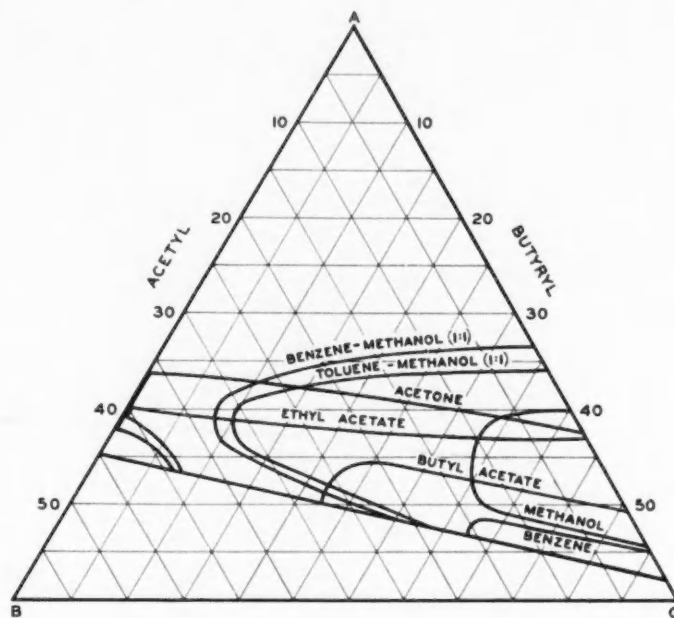


FIGURE 2—Chart showing solubility of cellulose acetate butyrate in various solvent combinations.

lack adequate moisture resistance or resin compatibility, or are not sufficiently soluble in hydrocarbons or oils; and where high tensile strength is not a primary factor. For general applications, a cellulose acetate stearate of approximately 35-40% stearyl content is satisfactory. Such a product has adequate tensile strength and surface hardness for average uses, will dissolve upon warming in toluene or benzene, and will be compatible with at least equal quantities of most of the common resins.

Esters of Dibasic Acids

Cellulose derivatives of quite different characteristics are obtained when one of the acids used in the esterification is dibasic. The most interesting of these mixed esters are those in which but one carboxyl group of the acid is combined with the cellulose, the other remaining as a free acid. Typical of this class is cellulose acetate hydrogen phthalate. The presence of acetyl groups gives the product an appreciable degree of water resistance and solubility in organic solvents, while the phthalic acid half ester results

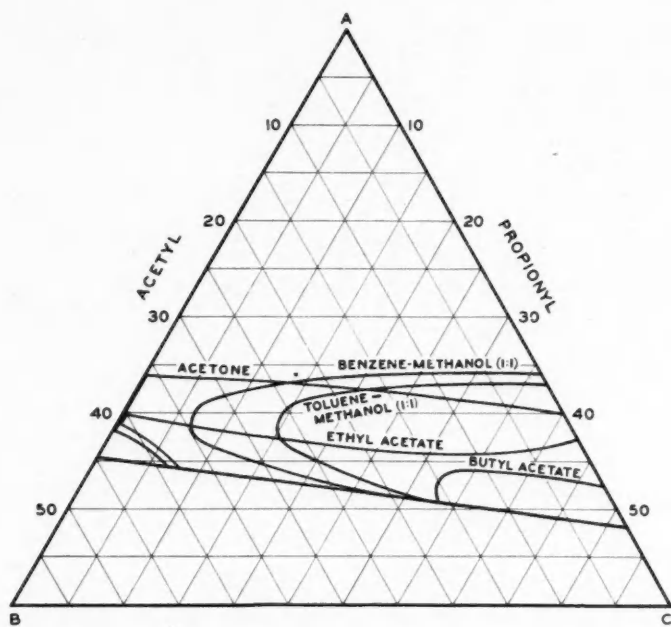


FIGURE 1—Chart showing solubility of cellulose acetate propionate in various solvent combinations.

genated solvents while partial hydrolysis increases the tolerance for alcohols. Hydrolysis also increases the ability of the ester, in combination with plasti-

in solubility in aqueous alkaline reagents by the formation of salts.

Thus, cellulose acetate hydrogen phthalate of 30-40% combined phthalic acid may be suspended in water and dissolved by the addition of sodium bicarbonate. In this manner, viscous aqueous solutions of the sodium salt in concentrations as high as 20-25% of the cellulose derivative may be prepared. By evaporation of these solutions, transparent, water-soluble films may be obtained, which at normal humidities are flexible, although when completely dried they become quite brittle unless a suitable water-soluble plasticizer has been incorporated therein.

Films or surface coatings of the acid form of cellulose acetate phthalate may be prepared from solutions in acetone, ethyl acetate, ethylene dichloride-alcohol mixtures, or other suitable solvents; they are resistant to water or acid solutions, but dissolve in dilute alkali.

Graphical Representation

Trilinear charts have been found most convenient for designation of the chemical composition of cellulose mixed esters. The composition in percentage acetyl

may be plotted along the *AB* axis, and the percentage of higher acyl along the *AC* axis. In the case of cellulose acetate butyrate, for example, the point at 44.8% on the *AB* axis will designate cellulose triacetate; and the point at 57.3% on the *AC* axis, cellulose tributyrate. A line connecting these points will indicate all fully esterified cellulose acetate butyrates of varying ratios of the two acyl groups. Points of lower total acyl values than these will represent partially hydrolyzed esters. Acetone-soluble cellulose acetate, a partially hydrolyzed ester, containing approximately 36-42% acetyl, will thus fall between points 36 and 42 on the *AB* axis.

On the accompanying triangular charts for cellulose acetate propionate, Figure 1, and cellulose acetate butyrate, Figure 2, are shown areas of solubility of the esters in a number of the more commonly employed organic solvents. From such charts it is possible to choose the chemical composition of cellulose ester most suitable for any particular use. It will be noted that within each group of esters the wider latitude of solubility in most solvents is found in those in which the higher acyl content is greater.

New Eastman Organic Chemicals

4665	2-Acetaminofluorene	4726	β,β -Diphenylpropionic Acid
4686	2-Amino-3,5-diiodobenzoic Acid	4607	α,d -Galacturonic Acid $\cdot 1H_2O$
4741	α -Aminopyridine	4774	Hydroxyethyl-ethylenediamine
4672	1,2-Benzanthracene	4448	Mannitol Hexaacetate
4724	β -Benzoylpropionic Acid	4676	<i>d</i> -neo-Menthol
4670	2-Bromo-1,4-dimethylbenzene	4688	4-Methyl-7-chlorohydrindene
4669	Bromo-tere-phthalic Acid	4648	α -Methylstyrene
4756	iso-Butylene Glycol	4695	Mono- <i>n</i> -butyrin
4574	<i>n</i> -Butyl <i>p</i> -Hydroxybenzoate	4703	Monopropionin
4725	2-Chlorobenzoxazole	4560	3-Nitro-2-iodotoluene
4630	β -Chlorobutyric Acid	4143	Phenoxyacetone
4654	β -Chloropropionyl Chloride	4765	<i>p</i> -iso-Propylbenzaldehyde
4742	Cholesteryl Propionate	4646	Resorcylaldoxime
4758	iso-Crotyl Chloride	4480	Sorbitol
4683	Dehydrobenzoylacetic Acid	4702	Tetra- <i>n</i> -butylammonium Iodide
4594	Dibenzothiophene	4697	Tetrapropylammonium Iodide
4588	3,4-Diethoxybenzaldehyde	4687	2,3,5-Triiodobenzoic Acid
4584	3,5-Dinitro- <i>o</i> -cresyl Acetate	4674	Zinc Methyl

The Packaging of Eastman Organic Chemicals



THE packing of chemicals may seem a prosaic operation, but with Eastman Organic Chemicals it is an extremely important step in supplying pure compounds. The primary object of the packaging is to insure the retention of the original condition of the material.

The properties, principally the reactivity or solvent action, of the more than 3,200 Eastman Organic Chemicals, vary widely, necessitating different types of closures and in some instances special containers. Glass bottles are employed almost exclusively since only by their use can the original purity of the products be maintained. Ground-glass stoppers, screw caps, rubber stoppers, and corks are all employed, the selection being made only after thorough tests, with each compound, of chemical inertness, tightness of closure, and ease of

opening. Low-boiling and certain lachrymatory or evil-smelling liquids are packed in sealed glass vials. Only compounds, mainly technical or practical grades, which because of their characteristics do not require glass are packaged in metal containers.

Because of the nature and cost of Eastman Organic Chemicals and the variety of package sizes, it is not practical to store them in packaged form. The compounds are kept in large glass bottles from which the amount required is removed and specially packaged for each order. This method, while time-consuming, provides an additional check on quality. Before packing, each chemical is examined for signs of decomposition which might have taken place during storage, an operation which could hardly be carried out with prepackaged items.